

PHOTOSENSITIVE BOTTOM ANTI-REFLECTIVE COATINGS

BACKGROUND OF THE INVENTION

5 Related Applications

 This application claims the priority benefit of a provisional application entitled PHOTOSENSITIVE BOTTOM ANTI-REFLECTIVE COATINGS, Serial No. 60/400,461, filed July 31, 2002, incorporated by reference herein.

10 Field of Invention

 The present invention is concerned with new anti-reflective compositions for use in photolithographic and semi-conductor integrated circuit manufacturing. In particular, the compositions are used as bottom anti-reflective coatings which become soluble in typical photoresist developing solutions upon exposure to light.

15 Background of the Prior Art

 The most common steps for removing bottom anti-reflective coatings from a substrate are wet and dry development processes. In the wet process, the bottom anti-reflective coating is exposed to an alkaline media which causes the polymer to dissolve.

20 Most wet developable bottom anti-reflective coatings are based on polyamic acid-imide chemistry. That is, the conversion of an acid (alkaline soluble) to an imide (alkaline insoluble) is the basis for controlling the ability to remove the film. This chemical change is thermally induced, and there is a bake window in which the bottom anti-reflective coating is insoluble in the resist solvent but soluble in alkaline media. The

25 main challenge with this process is maintaining and controlling the bake window to avoid scum (polymer residue) and to keep the bottom anti-reflective coating from being removed by the resist.

 In the dry development process, a high energy plasma - typically oxygen - removes the bottom anti-reflective coating. This process works well, but it requires an

30 additional processing step which increases the cost of manufacturing and throughput.

There is a need for improved bottom anti-reflective coatings which solve the problem of having to control a bake window and which eliminate the extra step required by dry development processes.

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SUMMARY OF THE INVENTION

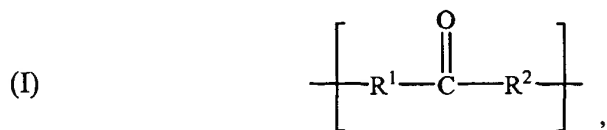
The present invention overcomes these problems by broadly providing novel polymers and bottom anti-reflective coatings which include those polymers.

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In more detail, the inventive polymers are selected from the group consisting of polycarbonates, polysulfonyl esters, and polycarbonate-sulfones (i.e., polymers which include recurring monomers having both an -SO₂ group and a -CO₃ group).

In embodiments where the polymer is a polycarbonate, preferred polycarbonates comprise recurring monomers having the formula

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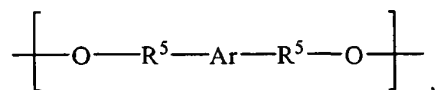


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where each of R¹ and R² is individually selected from the group consisting of functional moieties of diols, including aliphatic (preferably C₁-C₁₂) diols, aromatic (preferably C₄-C₁₂) diols, and heterocyclic diols). Preferred diols include those selected from the group consisting of bisphenols.

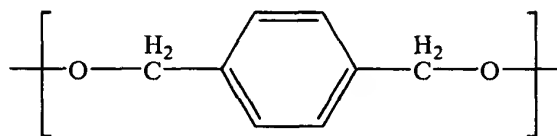
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In a preferred embodiment, at least one of R¹ and R² is selected from the group consisting of functional moieties of the bisphenols (and preferably bisphenol P and/or bisphenol Z). In this embodiment, it is preferred that the other of R¹ and R² has the formula

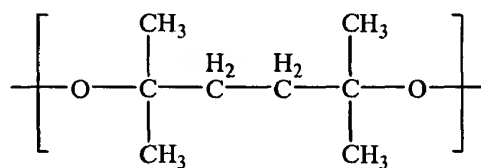


where R^5 is an alkyl group (substituted or unsubstituted, preferably C_1 - C_{12} , and more preferably C_1 - C_6), and Ar is an aryl group (substituted or unsubstituted, preferably at least C_4 , more preferably C_4 - C_{12} , and even more preferably C_6 - C_{10}).

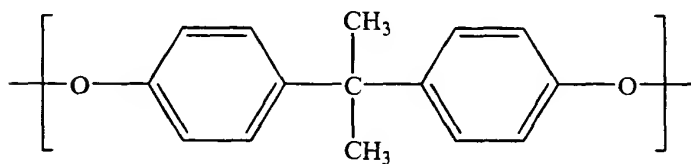
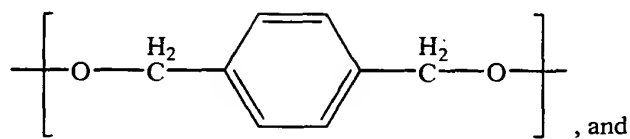
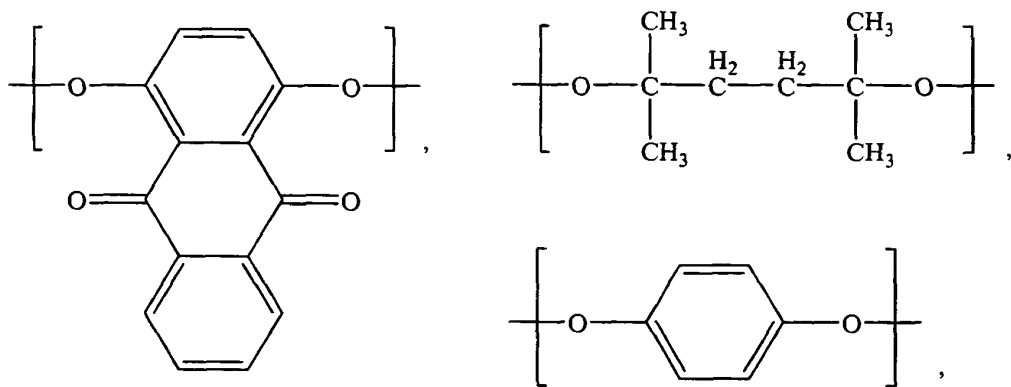
In another embodiment, when one of R^1 or R^2 is a moiety of bisphenol A, the other of R^1 and R^2 is a group other than



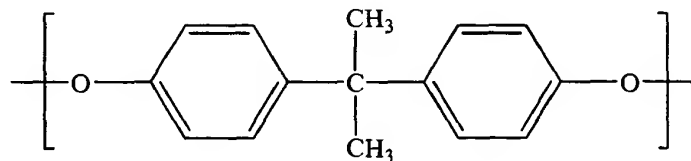
or



Particularly preferred R^1 and R^2 groups include those having a structure selected from the group consisting of

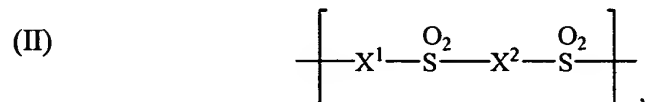


As used herein, the term "functional moiety" is intended to refer to moieties of compounds whose respective structures have been altered so that they may bond with other compounds. For example, the structure



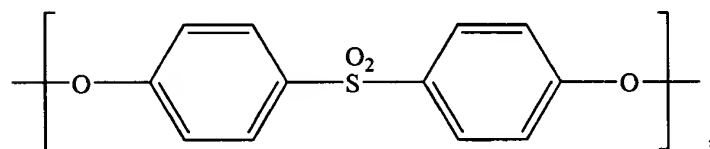
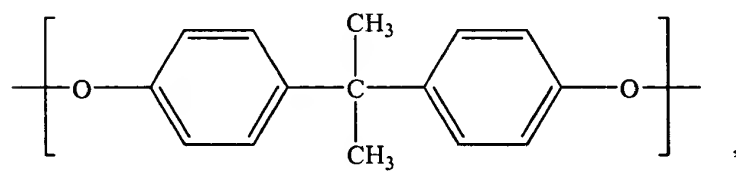
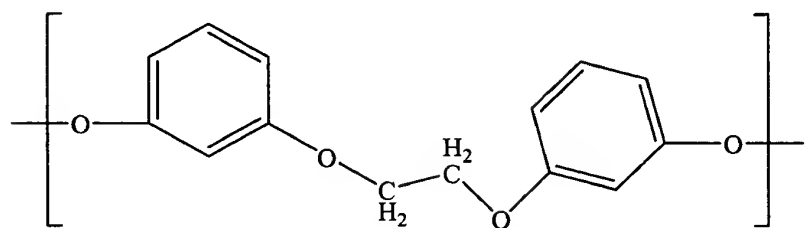
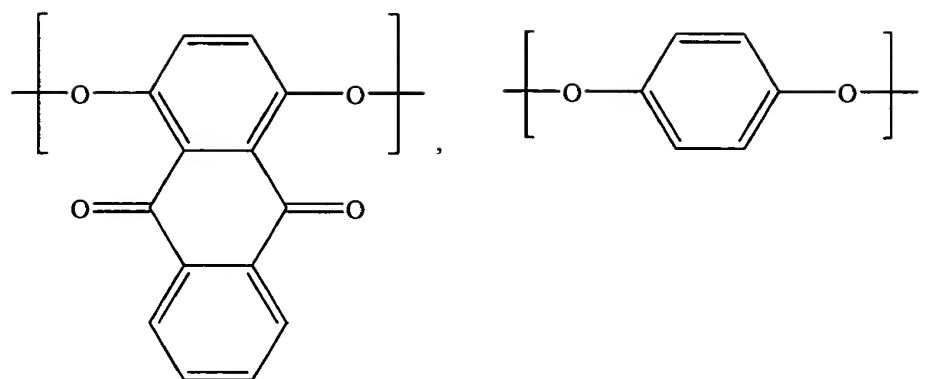
would be considered a functional moiety of bisphenol A, with the hydrogen atoms from each of the -OH groups originally present in the compound having been removed so that the oxygen atoms can bond with another compound or moiety.

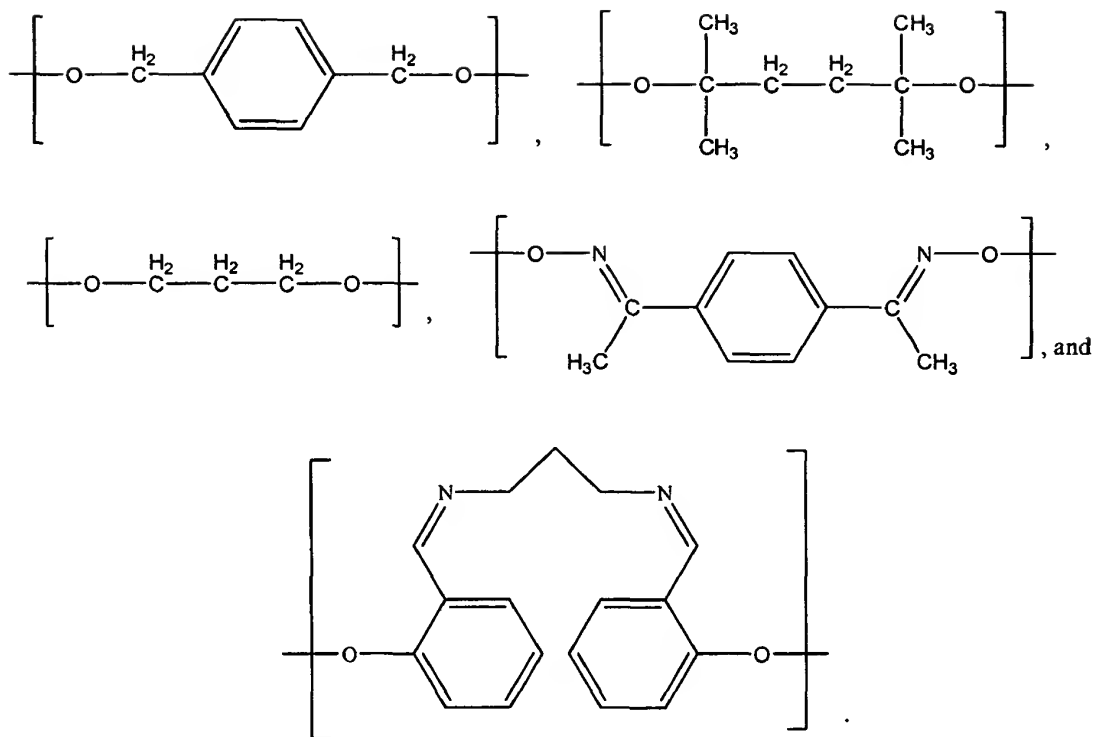
In embodiments where the polymer is a polysulfonyl ester, the polymer preferably has the formula



where X^1 is selected from the group consisting of functional moieties of diols and dioximes. Preferred diols include aliphatic (preferably C_1 - C_{12}) diols, aromatic (preferably C_4 - C_{12}) diols, and heterocyclic diols. Particularly preferred diols include those selected from the group consisting of the bisphenols. Preferred dioximes include aliphatic (preferably C_1 - C_{12}) dioximes, aromatic (preferably C_4 - C_{12}) dioximes, and heterocyclic dioximes. Particularly preferred dioximes include those derived from the condensation of an aliphatic diamine (NH_2 -carbon chain- NH_2) and substituted or unsubstituted hydroxybenzaldehydes and hydroxyacetyl benzenes. One particularly preferred example is 1,4-diacetyl benzene dioxime.

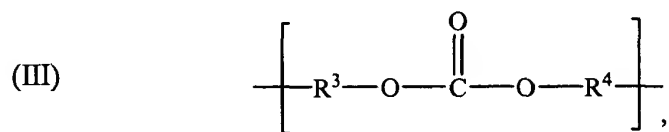
In a preferred embodiment, X^1 has the formula -O-Z-O- where Z is selected from the group consisting of substituted and unsubstituted aryls (preferably at least C_4 , more preferably C_4 - C_{12} , and even more preferably C_6 - C_{10}), substituted and unsubstituted alkyls (preferably C_1 - C_{12} , and more preferably C_1 - C_6), and combinations thereof. Particularly preferred X^1 groups have a structure selected from the group consisting of





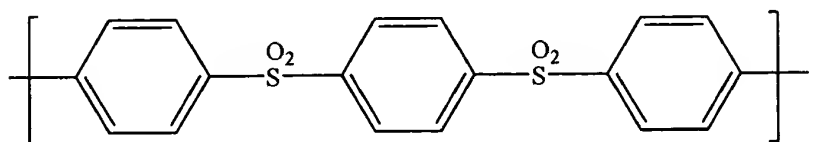
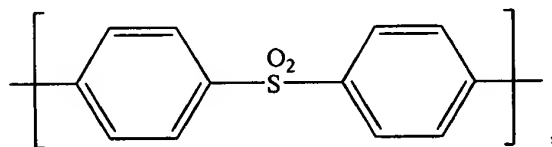
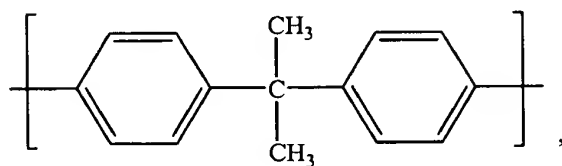
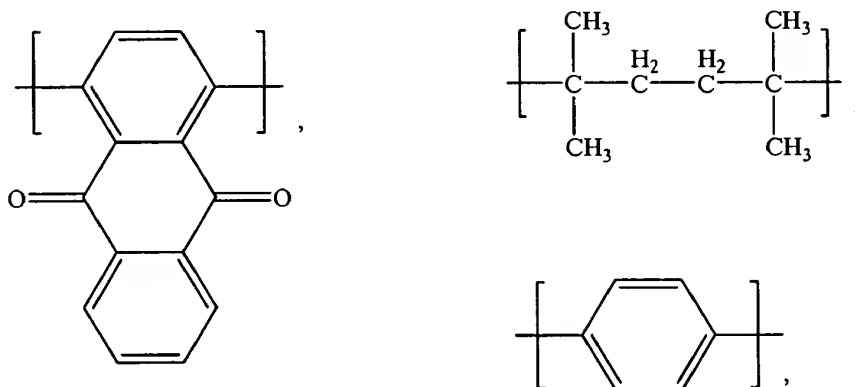
In formula (II), X^2 is selected from the group consisting of substituted and
 5 unsubstituted aryls (preferably at least C_4 , more preferably C_4-C_{12} , and even more
 preferably C_6-C_{10}) and substituted and unsubstituted alkyls (preferably C_1-C_{12} , and more
 preferably C_1-C_6). Particularly preferred X^2 groups include those selected from the group
 consisting of phenyls, naphthyls, furyls, thionyls, and anthranlys. It is preferred that at
 least one of X^1 and X^2 includes an aromatic portion or other light absorbing group.

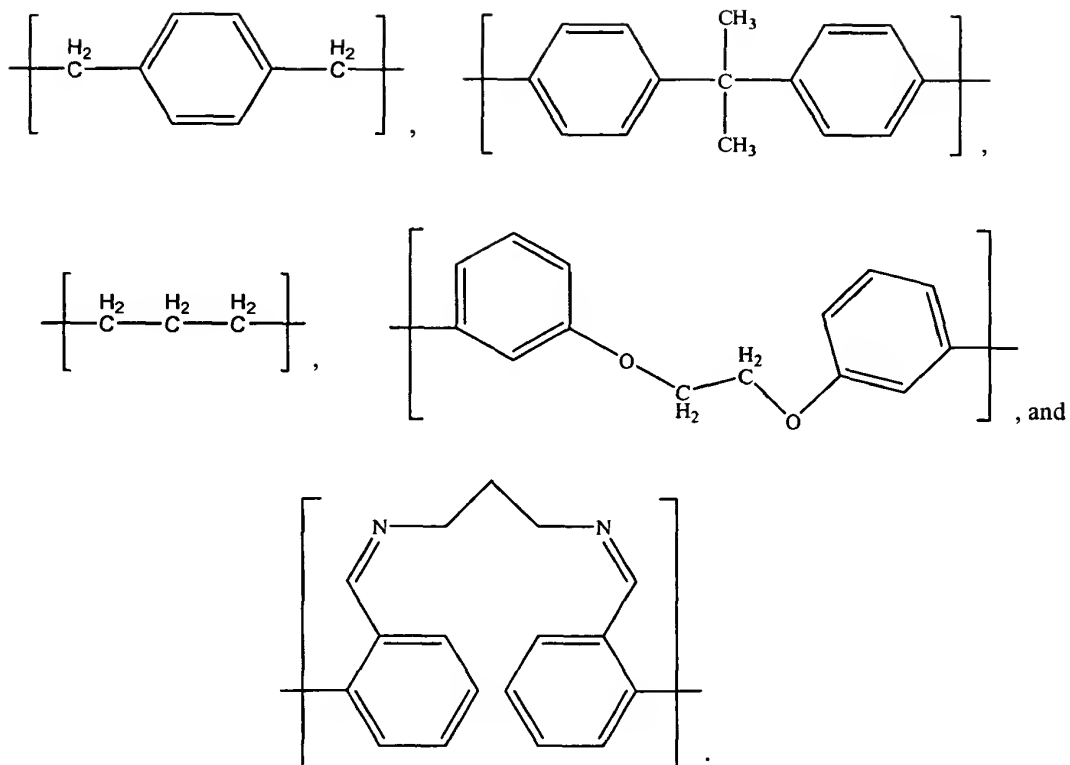
10 In embodiments where the polymer is a polycarbonate sulfone, a preferred
 structure for this polymer is



where each of R^3 and R^4 is individually selected from the group consisting of substituted and unsubstituted aryls (preferably at least C_4 , more preferably C_4 - C_{12} , and even more preferably C_6 - C_{10}), and alkyls (preferably C_1 - C_{12} , and more preferably C_1 - C_6).

At least one of R^3 and R^4 will include an $-SO_2$ group, and it is preferred that at least one of R^3 and R^4 includes an aromatic portion or other light absorbing group. Particularly preferred R^3 and R^4 groups include those selected from the group consisting of





5 Preferably, the polymer has an average molecular weight of from about 1,000-100,000 Daltons, more preferably from about 2,000-50,000 Daltons, and even more preferably from about 2,000-20,000 Daltons.

10 These polymers can be utilized to make compositions (e.g., anti-reflective coatings) for use in microlithographic processes. The compositions are formed by simply dispersing or dissolving the polymer(s) in a suitable solvent system, preferably at ambient conditions and for a sufficient amount of time to form a substantially homogeneous dispersion. Preferred compositions comprise from about 1-20% by weight polymer, and preferably from about 2-10% by weight polymer, based upon the total weight of the composition taken as 100% by weight.

The solvent systems can include any solvent suitable for use in the microelectronic manufacturing environment. Preferred solvent systems include a solvent selected from the group consisting of propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), ethyl lactate, propylene glycol, n-propyl ether (PnP), cyclohexanone, γ -butyrolactone, and mixtures thereof. The solvent should be present in the composition at a level of from about 80-98% by weight, based upon the total weight of the composition taken as 100% by weight. Preferably, the solvent system has a boiling point of from about 100-160°C.

Any additional ingredients are also preferably dispersed in the solvent system along with the polymer. Examples of suitable additional ingredients include crosslinking agents, catalysts (e.g., photoacid generators or "PAGs"), and surfactants. Preferred crosslinking agents include aminoplasts (e.g., POWDERLINK® 1174, Cymel® products), multifunctional epoxy resins (e.g., MY720, CY179MA, DENACOL), anhydrides, and mixtures thereof. When used, the crosslinking agent is present in the composition at a level of from about 10-50% by weight, and preferably from about 15-30% by weight, based upon the total weight of the solids in the composition taken as 100% by weight.

Suitable PAGs include both ionic and nonionic PAGs. Examples of particularly preferred PAGs include sulfonic acid-type PAGs such as those sold under the names CGI 261, CGI 1397, and CGI 1311 (CIBA Specialty Chemicals). When used, the PAG should be present in the composition at a level of from about 0.05-10% by weight, and preferably from about 2-8% by weight, based upon the total weight of the solids in the composition taken as 100% by weight.

The method of applying the inventive anti-reflective compositions to a substrate (e.g., silicon, aluminum, tungsten, tungsten silicide, gallium arsenide, germanium, tantalum, SiGe, and tantalum nitride wafers) simply comprises applying a quantity of a composition hereof to the substrate surface (either a planar surface or one comprising vias or holes formed therein) by any conventional application method, including spin-coating. The layer should then be heated to at least about the crosslinking or curing temperature of the composition (e.g., about 80-180°C) so as to cure or harden the layer which can be formulated to have a thickness of anywhere from about 300-2,000 Å (less than the

thickness of the photoresist layer), where the thickness is defined as the average of 5 measurements taken by an ellipsometer.

The refractive index (n value) of the cured anti-reflective layer or coating will be at least about 1.4, and preferably from about 1.4-1.7 at a wavelength of about 193 nm. Furthermore, the OD of the cured layer will be at least about 2/μm, and preferably at least about 5/μm at a wavelength of about 193 nm. Stated another way, the cured anti-reflective layer will absorb at least about 80%, preferably at least about 90%, and more preferably at least about 95%, of light at a wavelength of about 193 nm when the layer is about 400 Å thick.

It will be appreciated that, at this stage in the process, the cured layers are substantially insoluble in solvents (e.g., ethyl lactate, propylene glycol monomethyl ether acetate) typically used in conjunction with photoresists. Furthermore, the cured layers are substantially insoluble in typical photoresist developers (e.g., alkaline developers such as tetramethylammonium hydroxide (TMAH)). In either instance, the thickness of the layer will change by less than about 10%, preferably less than about 5%, and more preferably by about 0% after contact with the photoresist solvent or the developer. As used herein, the percent change is defined as:

$$100 \cdot \frac{|(\text{thickness prior to solvent contact}) - (\text{thickness after solvent contact})|}{(\text{thickness prior to solvent contact})}$$

A photoresist can be applied to the cured material, followed by exposing thereof to light or activating radiation having the desired wavelength (e.g., wavelengths of from about 150-500 nm). Upon exposure to light, the cured anti-reflective layer will undergo a chemical change, thus causing the layer to be soluble in typical photoresist developers. That is, the cured compositions can, at this stage, be substantially (and preferably completely) removed with conventional aqueous developers such as TMAH and alkaline metal developers. Some of these developers are commercialized under the tradenames MF-319 (available from Shipley, Massachusetts), MF-320 (available from Shipley), and

NMD3 (available from TOK, Japan) developers. At least about 90%, and preferably at least about 99% of the inventive coatings will be removed by a base developer such as tetramethyl ammonium hydroxide and KOH developers. This percent solubility in commercially-available developers is a significant advantage over the prior art as this shortens the manufacturing process and makes it less costly.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXAMPLES

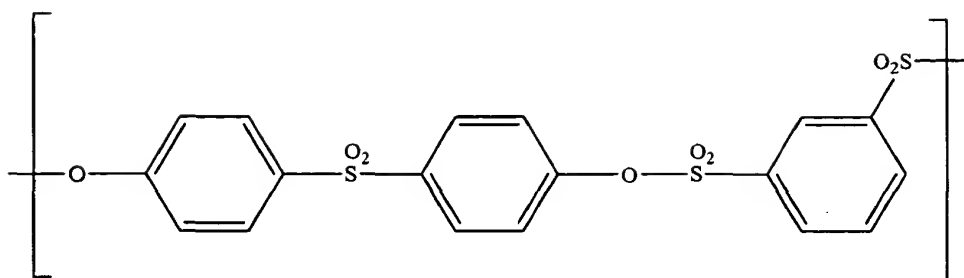
The following examples set forth preferred methods in accordance with the invention. It is to be understood, however, that these examples are provided by way of illustration and nothing therein should be taken as a limitation upon the overall scope of the invention. Unless stated otherwise, all materials in these examples were purchased from Aldrich Chemical Company and used as received.

EXAMPLE 1

Synthesis of Polysulfonyl Ester

As one example, polysulfonyl esters according to the invention can be prepared by condensation of an aromatic diol and benzene disulfonyl chloride. In this procedure, a 100 ml, round-bottomed flask, sulfonyl diphenol (bisphenol S, 1.82 g), 1,3-benzenedisulfonyl chloride (2.0 g), and dichloromethane (40 ml) were mixed and stirred at room temperature. Pyridine (1.2 ml) was added at once, and the mixture was heated to reflux for 24 hours. The reaction was allowed to cool to room temperature, the solvent was concentrated to about 10 ml, and the polymer was precipitated into methanol (200 ml). A 2.73 g (83%) quantity of a white polymer was collected. FT-IR and elemental analysis were consistent with the proposed structure. The molecular weight obtained was 2,747. The structure of the resulting polymer is shown in Structure A.

Structure A



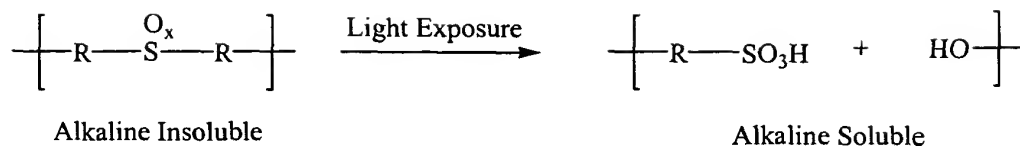
EXAMPLE 2

Formulation of Coating

The polymer prepared in Example 1 was dissolved in 10 ml of a cyclohexanone (4%) solution. The resulting solution was spin-coated (1500 rpm) onto a silicon wafer and bake dried at 175°C for 60 seconds. The baked film was immersed in a 0.25 N solution of TMAH but it could not be removed from the wafer by the TMAH. The film was subsequently exposed to a DUV source, and it was then soluble in a 0.25 N solution of TMAH. This indicates that the film underwent a chemical change upon exposure to DUV light. That is, upon exposure to light, the photoreactive linkage broke down and produced a sulfonic acid (-SO₃H-) which caused the polymer to become alkaline soluble. A generic reaction scheme showing the chemical change is depicted in Scheme 1.

The optical properties of the film were determined, and the film showed high absorbance at 193 nm (OD 21.4/μm) and moderate absorbance at 248 nm (OD 5.6/μm). This formulation could also be modified by adding a melamine or glycouril crosslinker (about 25-50% by weight).

Scheme 1



where:

R=light absorbing chromophore

X=2 or 3

EXAMPLE 3

Synthesis of Polycarbonate

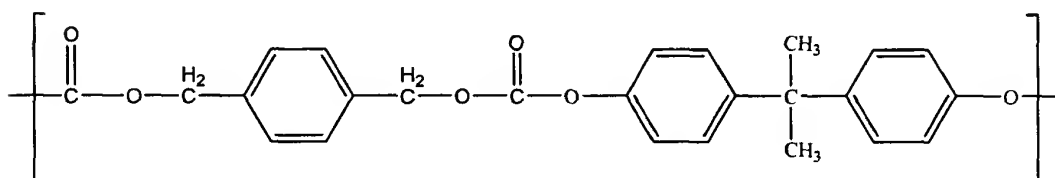
Polymers according to the invention can be prepared, for example, by reacting a bisphenol monomer with a diol containing a nitrophenol leaving group, with the condensation polymerization process being carried out in refluxing chloroform. White et al., Synthesis and Characterization of Photodefinable Polycarbonates for Use as Sacrificial Materials in the Fabrication of Microfluidic Devices, *Proc. SPIE*, **4690**, 242-253 (2002); Martin et al., A Convenient Laboratory Preparation of Aromatic Polycarbonates, *Polymer Bulletin*, **47**, 517-520 (2002), each incorporated by reference herein.

In this procedure, the synthesis of polycarbonates was carried out in two steps. First, the monomer was prepared by adding (over a one-hour time period) a solution of 2.0 g of 4-nitrophenylchloroformate in 10 ml dry dichloromethane to a solution of 0.68 g 1,4-benzene dimethanol in 0.8 ml of dry pyridine and 30 ml of dry dichloromethane. The reaction mixture was refluxed overnight followed by cooling to room temperature. Sufficient CH_2Cl_2 was added to dissolve the suspension formed, and the solution was washed once with 100 ml distilled water, once with 5% HCl solution, and once more with distilled water. The organic layer was dried over magnesium sulfate after which it was filtered, and the solvent was removed by a rotary evaporator. The white solid product was recrystallized using dichloromethane and petroleum ether (10:1), thus yielding the desired monomer.

This monomer (2.0 g) was mixed with bisphenol A (0.97 g), potassium carbonate (2.72 g), a catalyst (18-crown-6, 0.13 g), and chloroform (75 ml) in a 250 ml, round-bottomed flask. The mixture was heated to reflux for 50 hours. The reaction mixture was allowed to cool to room temperature, the inorganic salts were filtered off, the filtrate was concentrated to about 20 ml, and the polymer was precipitated into methanol (200 ml). A white polymer (1.58 g, 89%) was collected. FT-IR and elemental analysis were consistent with proposed structure. The molecular weight obtained was 5,641. The structure of the resulting polymer is shown in Structure B.

In other procedures, other bisphenols were used, and higher molecular weights were obtained.

Structure B



EXAMPLE 4

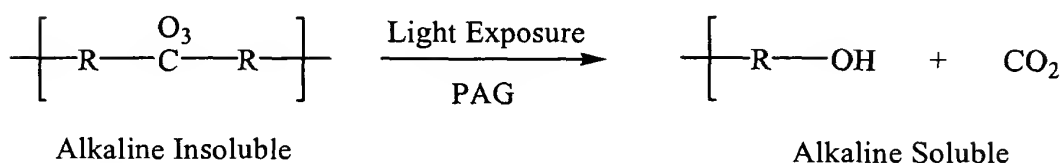
Formulation of Coating

The polymer (0.2 g) prepared in Example 3 was mixed with 0.04 g of CGI 1311 (a PAG, obtained from CIBA Specialty Chemicals) in 14 ml of PGMEA. The resulting solution was spin-coated (1500 rpm) onto a silicon wafer and bake dried at 100°C for 60 seconds. The baked film was immersed in a 0.25 N solution of TMAH but it could not be removed from the wafer by the TMAH. The film was subsequently exposed to a DUV source, and it was then soluble in a 0.25 N solution of TMAH. This indicates that the film underwent a chemical change upon exposure to DUV light. That is, the carbonate linkage reacted with an acid (produced by the PAG upon exposure to light in this instance), thus decomposing and forming CO₂ and an alcohol. The composition became alkaline soluble. A generic reaction scheme showing the chemical change is depicted in

Scheme 2.

The optical properties of the film were determined, and the film showed high absorbance at 193 nm (OD 24/ μm).

Scheme 2



where R=light absorbing chromophore

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EXAMPLE 5

Synthesis of Polycarbonate Sulfone

One method by which these polymers can be prepared is similar to that described in Example 3.

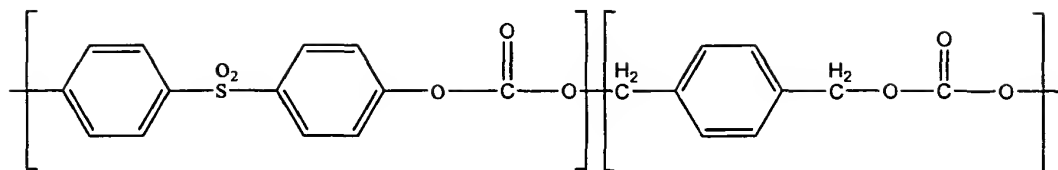
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In this procedure, the same monomer (4.68 g) prepared in Example 3 was reacted with bisphenol S (2.51 g), triethyl amine (2.79 ml), and dimethylamino pyridine (DMAP, 0.14 g) in acetonitrile (50 ml). The mixture was heated to reflux for 18 hours and then allowed to cool at room temperature. The solution was concentrated to about 15 ml and precipitated into methanol (125 ml). After drying overnight in a vacuum oven, 2.67 g (61%) of a yellow solid was collected. FT-IR and elemental analyses were consistent with the proposed structure. The structure of the resulting polymer is shown in Structure C.

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Structure C



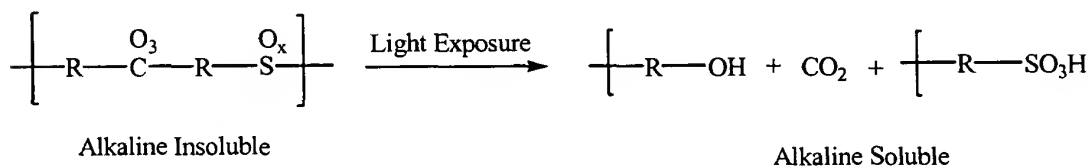
EXAMPLE 6

Formulation of Coating

The polymer prepared in Example 5 (0.4 g) was dissolved in 10 ml of a cyclohexanone (4%) solution. The resulting solution was spin-coated (1500 rpm) onto a silicon wafer followed by bake drying at 175°C for 60 seconds. The baked film was immersed in a 0.25 N solution of TMAH but it could not be removed from the wafer by the TMAH. The film was subsequently exposed to a DUV source, and it was then soluble in a 0.25 N solution of TMAH. This indicates that the film underwent a chemical change upon exposure to DUV light. That is, upon exposure to light, the photoreactive linkage broke down and produced a sulfonic acid (-SO₃H-) which caused the carbonate linkage to decompose and become alkaline soluble. A generic reaction scheme showing the chemical change is depicted in Scheme 3.

The optical properties of the film were determined, and the film showed high absorbance at 193 nm (OD 20.6/μm).

Scheme 3



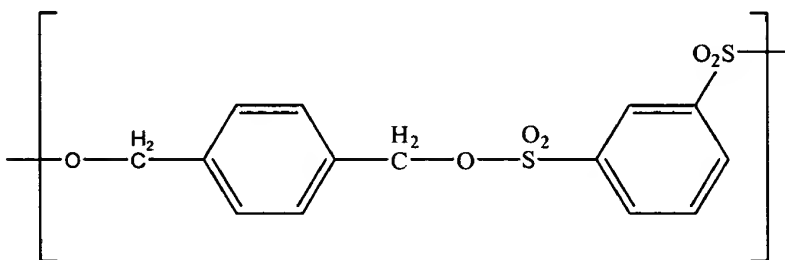
where:
R=light absorbing chromophore
x=2 or 3

EXAMPLE 7

Synthesis of Polysulfonylester

In a 250 ml, round-bottomed flask, benzenedimethanol (2.82 g) in 25 ml of tetrahydrofuran (THF) was treated with a 1M solution of potassium t-butoxide (41 ml) and stirred at room temperature for 10 min. A THF solution of 1,3-benzenedisulfonyl chloride (5.62 g in 25 ml of THF) was then added in portions to the reaction flask. The mixture was heated to reflux for 24 hours. The inorganic salts were then filtered, and the THF was removed under vacuum. The remaining residue was re-dissolved in chloroform (12 ml) and precipitated into methanol (150 ml). The precipitate was filtered and dried in a vacuum oven overnight. A white solid (0.90 g) was collected. The structure of the resulting polymer is shown in Structure D.

Structure D

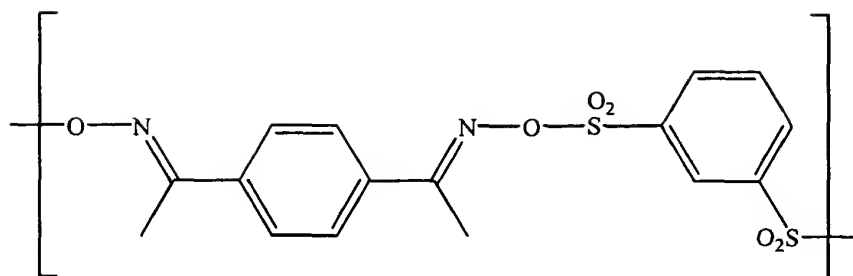


EXAMPLE 8

Synthesis of Polysulfonylester Oxime

In a 200 ml, round-bottomed flask, diacetylbenzene oxime (5.66 g) and triethyl amine (6.00 g) in chloroform (50 ml) were stirred at room temperature. Next, 1,3-benzenedisulfonyl chloride (8.08 g) was added in portions to the reaction flask. After stirring at room temperature for 30 minutes, the mixture was heated to reflux for 24 hours. The polymer precipitated out of the reaction mixture, and it was collected by filtration. After drying in a vacuum oven, 6.0 g of a brown polymer was collected. The structure of the resulting polymer is shown in Structure E.

Structure E



EXAMPLE 9

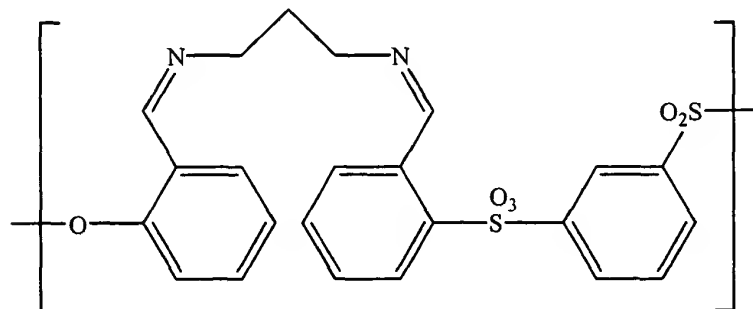
Synthesis of Polysulfonylester Imine

10 In this example, all materials were purchased from TCI and used as received. In a 250 ml, 2-neck, round- bottomed flask, N,N-disalicylal-1,2-propanediamine (3.00 g), 1,3-benzenedisulfonyl chloride (2.92 g), and chloroform (40 ml) were mixed and stirred

15 at room temperature. Triethyl amine (2.95 ml) was added in portions, and the mixture was heated to reflux for 23 hours. The reaction mixture was allowed to cool to room temperature, the solvent was concentrated to about 15 ml, and the polymer was precipitated into methanol (250 ml). The polymer was collected, redissolved in chloroform (15 ml), and precipitated one more time into methanol (200 ml). After drying

20 in a vacuum oven, 3.71 g (72%) of a yellow polymer was collected. The structure of the resulting polymer is shown in Structure F.

Structure F



EXAMPLE 10

Formulation of Coating

5 The polymer prepared in Example 9 was dissolved in 10 ml of a 4% solution of ethyl lactate. The resulting solution was spin-coated (1,500 rpm) onto a silicon wafer and then bake dried at 150°C. The baked film was immersed in a 0.25 N solution of TMAH but it could not be removed from the wafer by the TMAH. The film was subsequently exposed to a DUV source, and it was then soluble in a 0.25 N solution of TMAH. This indicates that the film underwent a chemical change upon exposure to DUV light and, therefore, is photosensitive.

10 The optical properties of the film were determined, and the film showed high absorbance at 193 nm (OD 14.4/ μm) and moderate absorbance at 248 nm (OD 5.53/ μm), thus making it suitable for anti-reflective applications.

15 The above formulation can also be modified by adding a melamine or glycouril crosslinker (about 5-50% by weight) and a photoacid generator (about 1-10% by weight).